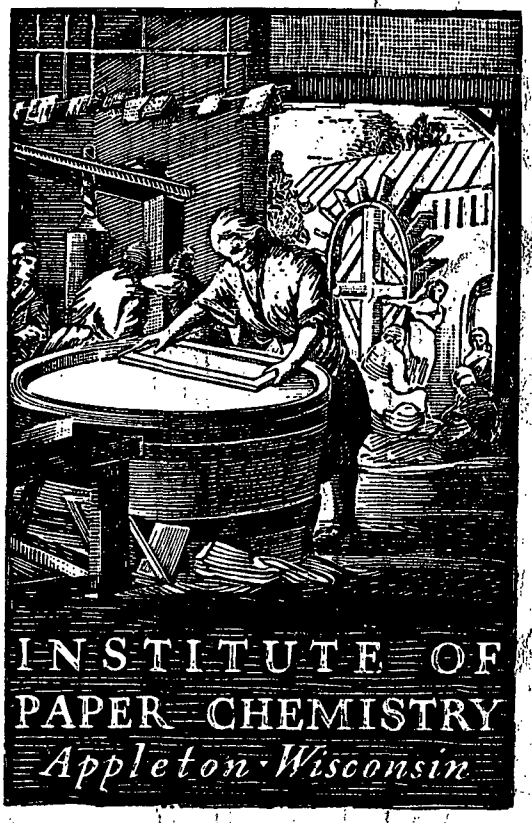

AUTOMATIC INSTRUMENTATION FOR CHEMICAL ANALYSIS OF PULP

Project 2634

Report Two

A Progress Report

to

MEMBERS OF GROUP PROJECT 2634

October 12, 1967

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

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October 12, 1967

Members of Group Project 2634:

Abitibi Paper Company Ltd.

Albemarle Paper Company

Badger Paper Mills, Inc.

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THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

AUTOMATIC INSTRUMENTATION FOR CHEMICAL ANALYSIS OF PULP

SUMMARY

As a supplement to the data presented in Report One, the regression relationship, Klason lignin vs. Nu number, is given for commercial unbleached softwood kraft pulps. The data show about the same relative error (ca. 4%) as for Kappa number vs. Klason lignin and Kappa number vs. Nu number.

Over a period of several days at a sponsoring mill, Nu numbers were determined on the same sample taken for routine K number measurement in order to determine the industrial applicability of the manual Nu number procedure. The relative error of the regression relationship, K number vs. Nu number, was 7.7%, while that of Kappa number vs. Nu number was 5.2%. No particular advantage was found in the Nu number procedure over the K number method when manually used. The Nu number method is, however, highly adaptable to automation, while the K number method is not.

Laboratory cooks of gum and aspen were made, using the neutral sulfite process, and for both woods a linear relationship was established between Nu number and yield. The relationship between Klason lignin and Nu number was definitely not linear. The yield range covered in these experiments was 56 to 100% (original wood).

Magnesium-base sulfite pulps were prepared in a yield range from 44 to 78% and analyzed for Klason lignin, Kappa number, and Nu number. The Kappa-Nu relationship was linear with a relative error of 3.6%.

Investigations of certain aspects of the compression characteristics of pads of pulp fibers in a water-saturated system were made to obtain initial design data for an automatic pulp sampler. The apparatus used was the Institute's compressibility tester, which produces 3-in. diameter pads. It was found that unbleached softwood kraft pulps have similar compression characteristics over a rather wide range of wood species and lignin contents. Over a compressing pressure range of 37.7-146 dynes/cm.^{2} and over a pad thickness range from 0.025 to 0.700 inch, it was found that the dry fiber content of the pads could be estimated from thickness measurements with a relative error of 2%. The overall time involved for the measurement is as little as three minutes for thin pads. Some experiments with neutral sulfite pulps in the 60-90% yield range show that while some of their compression characteristics differ from kraft pulps, the speed and accuracy of estimating fiber content from thickness of compressed pads is about the same.

A compressibility apparatus is presently under construction that will produce pads of 1.250 inches in diameter. This will permit the study of pads having equivalent dry fiber content of as little as 100 milligrams. The apparatus is so designed that compression studies can be made at temperatures other than ambient, and has additional design features that will permit reslurrying the compressed pad in the cylinder and carrying out the Nu number test in the compressibility apparatus.

INTRODUCTION

Report One, issued June 14, 1967, dealt mainly with investigations of various approaches to automatically measuring residual lignin in pulp and with the development of a simplified procedure involving reaction of nitric acid with pulp. This simplified procedure, called the "Nu number" method, has been selected for further development into an automated system.

It can be seen that in the overall program for development of an automated test for residual lignin in pulp there are at least two major phases of the work. One phase concerns the selection, development, and extensive technical examination of the test method itself. This phase is largely completed, as can be seen from a study of Report One.

A second phase of the work must deal with the development of an automatic quantitative method of pulp sampling that is compatible with the selected test method. This phase of the work is presently under way.

Perhaps a third phase would be the joining together of the testing and sampling methods in the design and construction of a prototype device for automated residual lignin testing in the mill. This phase is still some months in the future.

However, at this time, while the second phase is well under way, additional data have been obtained on the applicability of the Nu number method, and some preliminary studies have been completed on the proposed pulp-sampling method. Also, the data on commercial pulps presented in Report One have been used to give the regression relationship between Klason lignin and Nu number.

Table XXII on page 76 and Table XXIII on page 77 in Report One give the regression relationship between Kappa number and Klason lignin and between Kappa number and Nu number, respectively. However, the Klason lignin-Nu number regression was not calculated. Since this information was requested by several delegates to the technical meeting held July 18 at the Institute, the calculations were made and the results are presented in this report.

This report, then, can be regarded as an "interim" report, issued to provide additional information pertaining to the first phase of the project and also revealing some preliminary data concerning the second phase.

REGRESSION RELATIONSHIP BETWEEN KLASON LIGNIN AND NU NUMBER FOR COMMERCIAL PULPS

In Report One, dated June 14, 1967, Table XXII and Fig. 22 give experi-ıtal data for the regression relationship of Kappa number on Klason lignin, and ɔle XXIII and Fig. 23 give the same relationship for Kappa number on Nu number r commercial pulps.

While the analytical data had been obtained, the same type of relation-ip for Klason lignin on Nu number was not presented in Report One. At the quest of some of the sponsors, the regression relationship has been calculated d is presented here in Table I and in Fig. 1. It can be seen from Table I at the overall relative error is about the same as for Kappa on Klason and for ppa and Nu.

TABLE I

REGRESSION RELATIONSHIP OF KLASON LIGNIN ON NU NUMBER FOR COMMERCIAL PULPS

ll o.	No. of Tests	Regression Line	Corr. Coeff.	Standard Error of Est.	Rel. Error of Est.
1	17	% Kl = 0.108 + 0.073 Nu	0.872	0.21	5.8
2	14	% Kl = -2.14 + 0.123 Nu	0.966	0.34	3.7
3	11	% Kl = -0.875 + 0.117 Nu	0.987	0.09	1.8
4	12	% Kl = -0.406 + 0.116 Nu	0.989	0.26	5.8
5	12	% Kl = -1.37 + 0.115 Nu	0.975	0.22	3.0
6	12	% Kl = 0.360 + 0.080 Nu	0.954	0.18	3.0
7	12	% Kl = -4.10 + 0.126 Nu	0.795	0.90	5.8
ɔtal	90	% Kl = -0.756 + 0.105 Nu	0.987	0.30	4.2

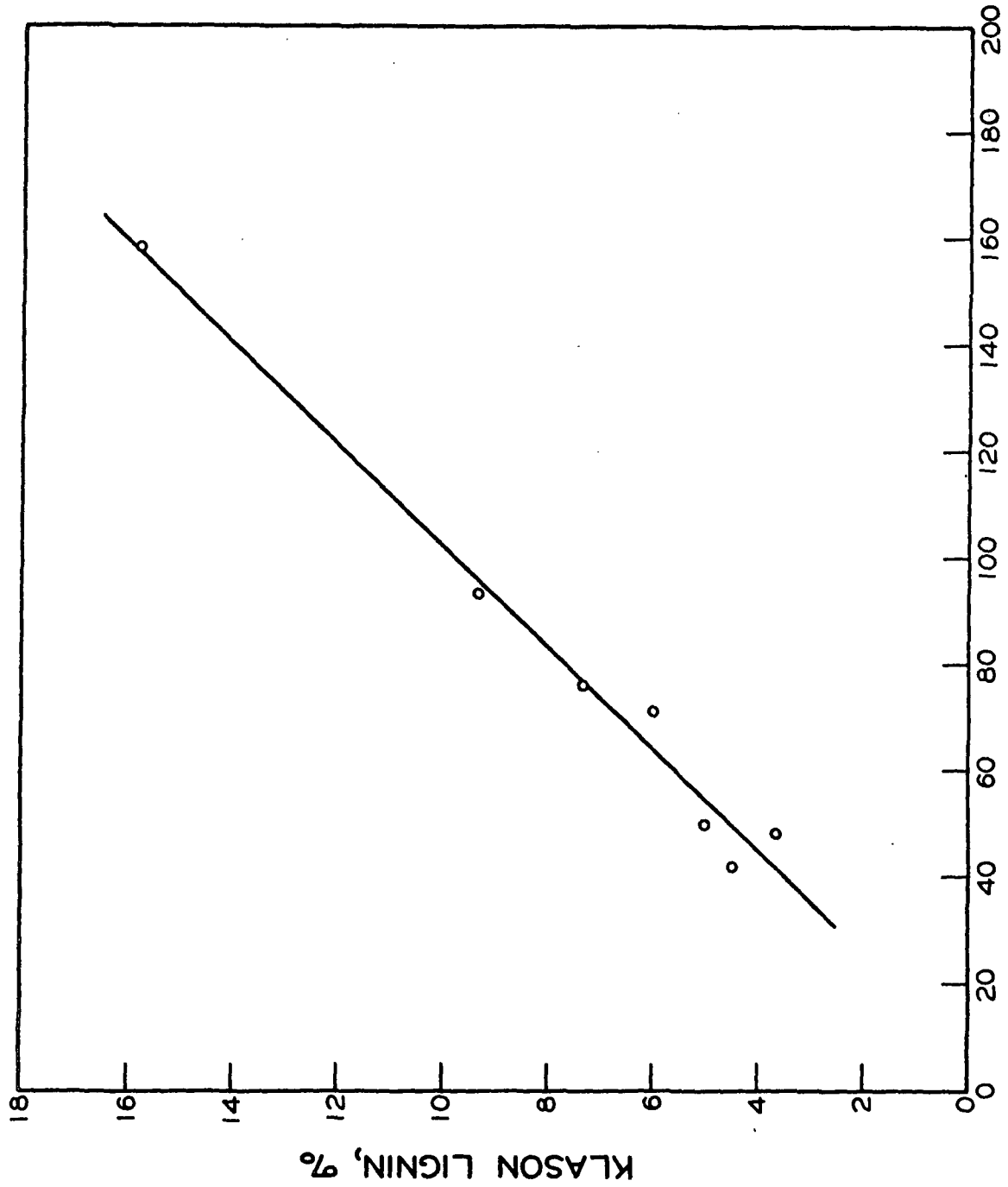

Figure 1. Regression Relationship of Klason Lignin on Nu Number for Commercial Pulps

INDUSTRIAL TRIAL OF THE NU NUMBER METHOD

To test the Nu number method in conjunction with operations in a pulp mill, some experiments were performed at a mill of one of the project sponsors. This mill was chosen because it made pulp of different yields simultaneously. The object of these experiments was to analyze fresh pulp samples for Nu number at the same time the mill permanganate numbers were determined.

The Nu number procedure developed in the laboratory requires heating 30 mg. of ground (40-mesh) sample for about 20 minutes with 50 ml. of 14% nitric acid at 70°C. Subsequent experiments have shown that identical results are obtained when unground samples are used. Further, it was found that the heating time can be reduced to 8 minutes when the temperature is increased to 80°C., using 100 mg. of sample.

The equipment used for these Nu number determinations was the same as described in Progress Report One, except that a Beckman Model B spectrophotometer was used for the photometric measurements.

The mill procedure for determining permanganate (K) number is as follows: A pulp suspension is made from a sample taken from the washer. One liter of the suspension is filtered and the pad is dried and weighed. The amount of suspension to be used for the permanganate number determination is read from a calibration table, depending upon the weight of the dried pad.

This dried pad was used for the Nu number determination. Duplicates of 100 mg. were weighed into 100-ml. beakers. Fifty ml. of 14% nitric acid were added and the beakers were placed for 8 minutes in an 80°C. water bath. After filtering off the fibers, the absorbance of the liquid was read at 425 nm. against

14% nitric acid as a blank, using 10-mm. cells. In all, 20 samples were taken during a two-day period. The remainder of the pads were brought to the Institute for determination of Kappa number.

In Table II are given the permanganate, Nu, and Kappa numbers. The regression line, correlation coefficients, and standard error of estimates were calculated for the combinations: Kappa vs. Nu, K vs. Kappa, and K vs. Nu. In Table III are given the calculated data. In Fig. 2 and 3 are plotted the data points and the calculated regression lines.

It can be seen from Table II that estimations of Kappa number from Nu numbers involve a relative deviation of 5.2% from the mean values established by the regression equation. In Report One, it was found that the deviation amounted to only 4.4% for commercial pulp. The only explanation for the increase is that considerable variations were observed in readings of the spectrophotometer. Examination of the instrument and experimentation with potassium dichromate standards indicated that absorbance readings were not at all reliable beyond the second decimal figure.

A second factor possibly contributing to the somewhat higher error involves an uncertainty in the amount of sample weighed out for the Nu number test. As already explained, the pad made by the mill employee and dried on the Noble & Wood hot plate for consistency measurement in conjunction with the permanganate number test was used for the Nu number measurement. Sometimes these dried pads were used as soon as they had cooled to room temperature, but other times as much as eight hours elapsed before samples of the pads were weighed out. It can be seen, then, that because of probable variations in moisture content, the amount of dry fiber in the samples weighed out for the Nu number test is subject

TABLE II

RESULTS OF ANALYSIS OF PULP SAMPLES OF INDUSTRIAL TRIAL OF NU NUMBER

Sample	K No.	Kappa No.	Nu No.
1	27.7	43.2	67
2	37.4	58.6	91
3	26.6	38.9	66
4	41.3	58.3	93
5	27.2	35.5	60
6	48.7	69.2	96
7	31.7	49.7	76
8	46.1	67.9	106
9	32.8	50.8	85
10	48.5	67.6	102
11	45.3	66.3	106
12	33.8	52.5	83
13	44.6	67.9	99
14	32.5	52.3	82
15	47.1	67.3	100
16	29.9	47.0	73
17	27.8	45.5	77
18	20.5	29.5	52
19	48.0	72.4	105
20	27.5	42.6	63

TABLE III

STATISTICAL DATA FOR INDUSTRIAL TRIAL RESULTS

Relation	Regression Equation	Coeff.	Error	Rel. Error, %
K-Kappa	Y = -1.64 + 0.70 X	0.979	1.9	5.3
K-Nu	Y = -7.67 + 0.523 X	0.954	2.8	7.7
Kappa-Nu	Y = -8.00 + 0.74 X	0.977	2.8	5.2

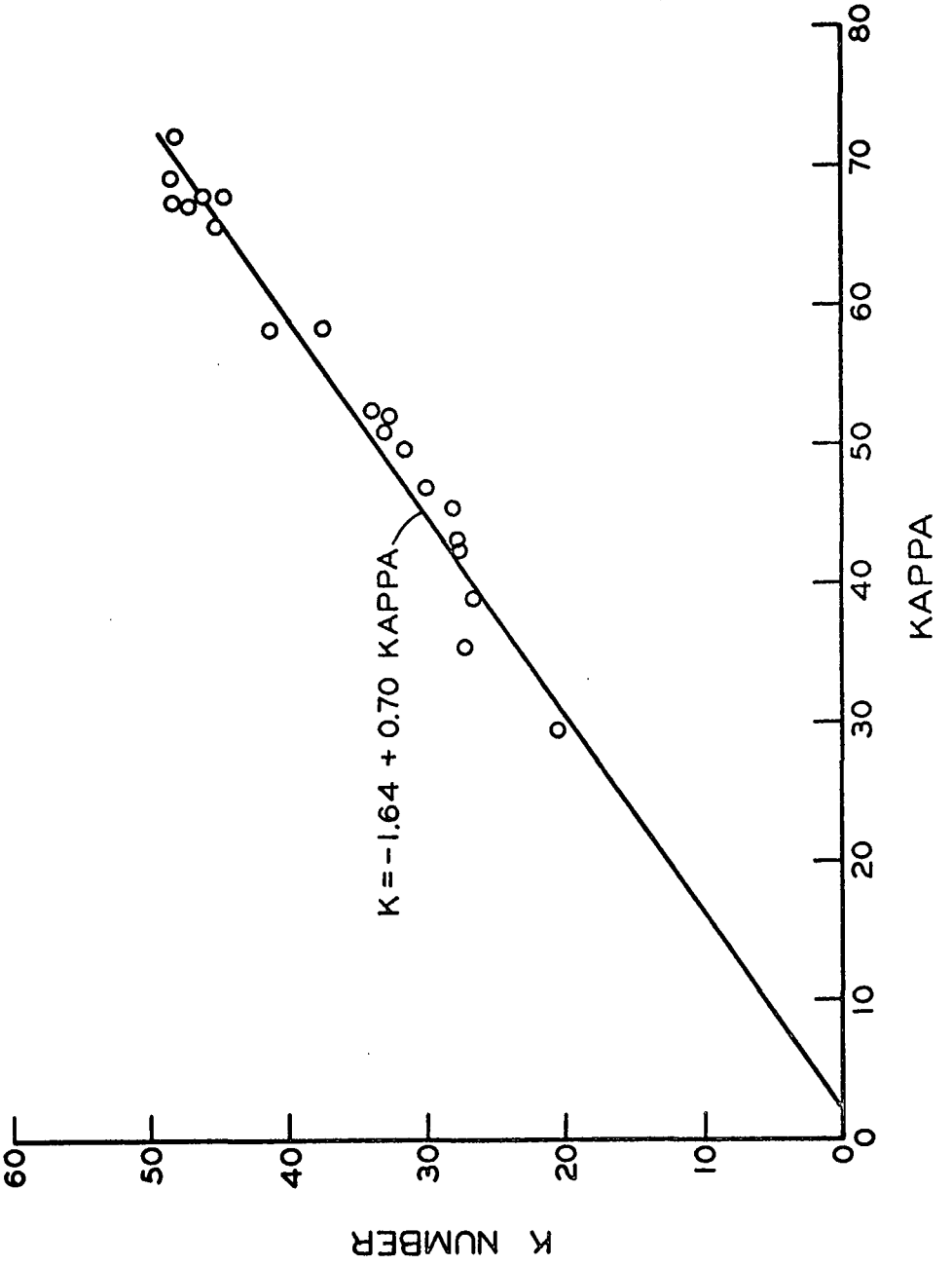

Figure 2. Regression Relationship, K No. vs. Kappa No., for Industrial Trial Pulps

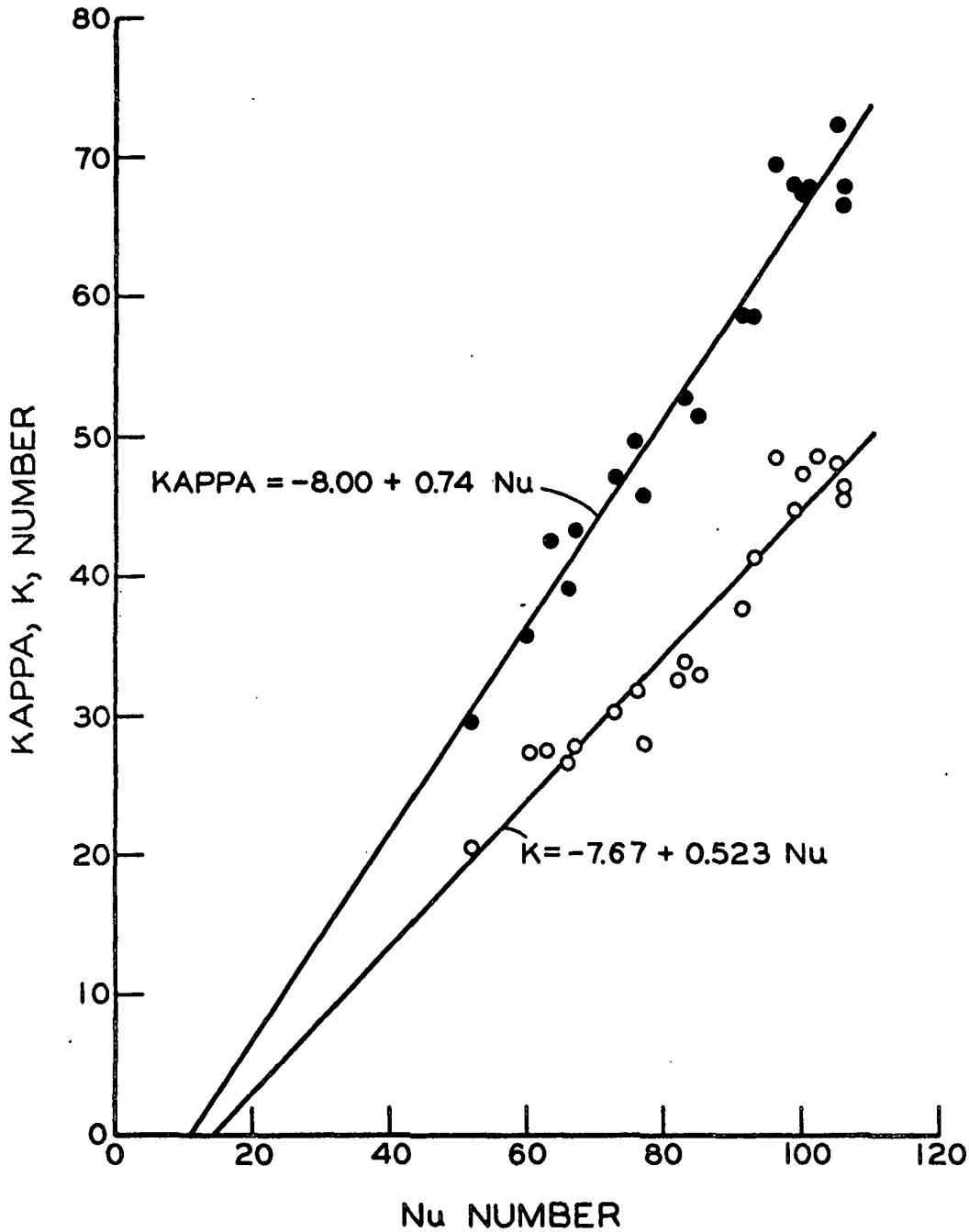

Figure 3. Regression Relationships, Kappa No. vs. Nu No. and K No. for Industrial Trial Pulps

to some uncertainty. However, because of the techniques involved, it is probable that an equal uncertainty exists in the samples routinely taken in the mill for K number measurements.

From this experience it was found that there is probably no overall advantage of the Nu number method over the K number method when both are performed manually. The Nu number method was, of course, developed specifically for eventual automation.

Manual use of the Nu number method requires weighing the dried sample on an analytical balance, the use of a constant-temperature bath to carry out the reaction, and a colorimeter for the final measurement. Only one reagent is required, however, and that one (14% HNO_3) is stable and very simple to prepare, mainly because it need not be standardized for accuracy.

The K number method requires no instruments, but does involve the use of three standardized reagents, two of which are not very stable. Because of the necessity of determining titration end points in the K number method, considerably more subjective error is inherent in its use than in the Nu number method.

Both the K number method and the Nu number method yield results in about the same period of time when performed manually.

APPLICATION OF THE NU NUMBER TO HIGH-YIELD NEUTRAL SULFITE AND TO MAGNESIUM-BASE SULFITE PULPS

NEUTRAL SULFITE

The Nu number method has so far been applied only to pulps with yield below 70%--that is, in the yield range where the Kappa number procedure is applicable. To test the suitability of the Nu number method for high-yield pulps, some cooks were performed in the multiunit digester described in Report One. Table IV shows the cooking conditions.

TABLE IV

CONDITIONS OF NEUTRAL SULFITE COOKS

Liquor composition: 15% Na_2SO_3, 4% Na_2CO_3 (based on wood)
Liquor-wood ratio: 6:1
Temp. = 175°C.

Cook	Wood	Cooking Time, min.
1	gum	7, 12, 17, 30, 90, 200
2	gum	20, 25, 40, 55, 130, 250, 300
3	aspen	17, 22, 27, 41, 55, 150, 300

The pulps were analyzed for Klason lignin and Nu number. The acid-soluble lignin formed during Klason lignin determination was determined according to an Institute procedure based on the absorbance at 208 nm. The analytical data are shown in Table V.

TABLE V

ANALYTICAL DATA OF NEUTRAL SULFITE PULPS

Wood Species Cooked	Cooking Time, min.	Yield, %	Klason Lignin, %	Acid-Sol. Lignin, %	Nu Number
Gum	0 (wood)	100	25.10	--	133
Gum	7	90.8	24.45	2.30	120
Gum	12	89.3	25.07	2.20	119
Gum	17	87.2	25.05	2.15	109
Gum	20	85.4	24.40	2.35	108
Gum	25	78.0	23.65	2.25	98
Gum	30	74.3	23.35	2.30	93
Gum	40	76.0	22.80	2.30	85
Gum	55	65.0	20.70	2.30	76
Gum	90	62.3	19.55	2.05	72
Gum	130	61.0	18.25	2.35	70
Gum	200	55.8	15.75	2.00	70
Gum	250	57.5	15.80	2.05	66
Gum	300	56.4	15.10	1.95	63
Aspen	0 (wood)	100	21.10	--	153
Aspen	17	87.8	21.10	1.95	128
Aspen	22	83.3	20.20	2.10	116
Aspen	27	82.0	20.20	1.90	113
Aspen	41	78.6	18.75	2.15	92
Aspen	55	75.5	17.75	1.90	84
Aspen	150	67.7	14.25	1.65	67
Aspen	300	64.0	11.25	1.55	58

In Fig. 4 Klason lignin is plotted against Nu number. There is no straight-line relationship between Klason lignin and Nu number, even when the acid-soluble lignin is included. The relationship between yield and Nu number, however, seems to be linear, as shown in Fig. 5.

The regression relationships, correlation coefficients, and standard errors of estimate were calculated, and the results are given in Table VI.

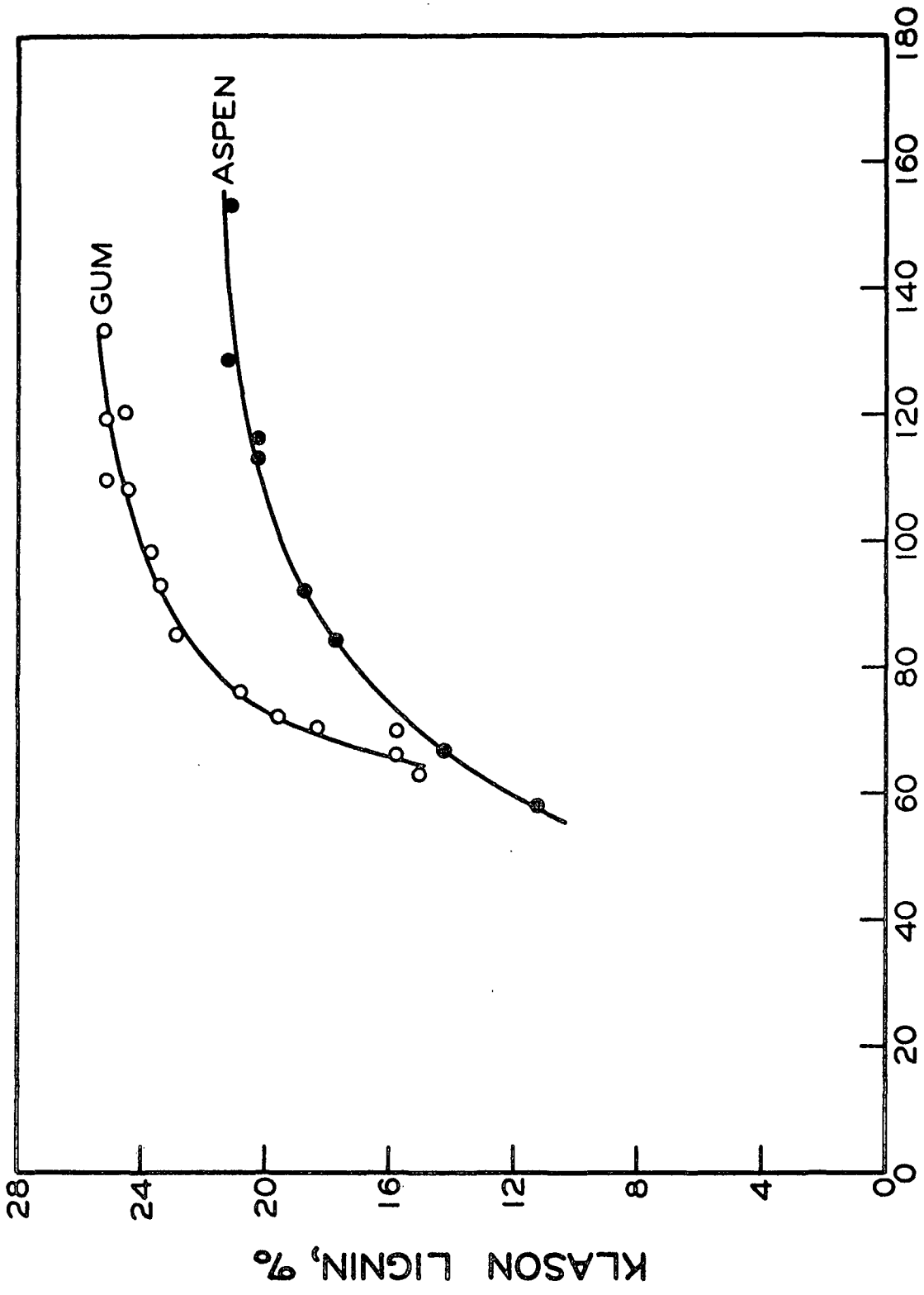

Figure 4. Klason Lignin vs. Nu Number of Neutral Sulfite Pulps

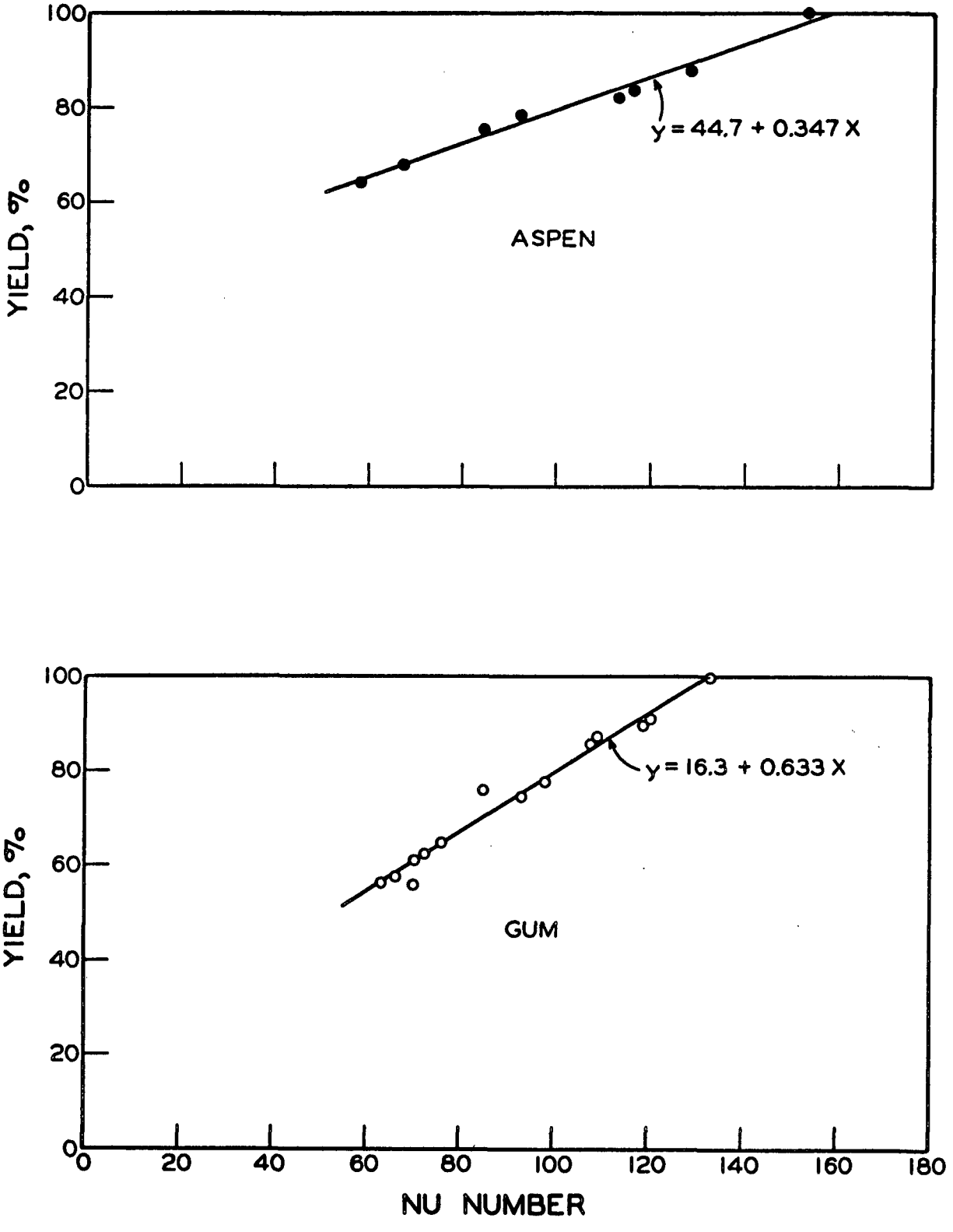

Figure 5. Percent Yield vs. Nu Number of Neutral Sulfite Pulps

TABLE VI

REGRESSION DATA ON NEUTRAL SULFITE PULPS

Wood	Cook	Regression Line	Corr. Coeff.	Std. Error	Rel. Error
Gum	N-S	Yield = 16.3 + 0.633 Nu	0.985	2.55	3.4%
Aspen	N-S	Yield = 44.7 + 0.347 Nu	0.980	2.20	2.7%

MAGNESIUM-BASE SULFITE

Some acid sulfite cooks were performed to produce pulps for testing the Nu number method. The only wood species used was black spruce. The first experiments were performed in the following manner: Two hundred grams of (ovendry basis) chips and 1600 ml. of liquor were placed in a stainless steel digester equipped with a pressure gage and immersed in an oil bath. The liquor composition was 59.79 SO_2 and 22.7 $Mg(OH)_2$ per liter. Five separate cooks were performed. In Table VII are given the conditions for this first series of cooks.

TABLE VII

CONDITIONS FOR FIRST SERIES OF SULFITE COOKS

Cook	Max. Temp., °C.	Time to Max. Temp., min.	Time at Max. Temp., min.	Total Time, min.
1	142	285	0	285
2	145	270	180	450
3	145	240	120	360
4	160	195 (to 145°)	135 at 145°, 45 at 160°	375
5	145	285	300	585

The pulps were analyzed for yield, Klason lignin, and Nu number. The results are given in Table VIII.

TABLE VIII

ANALYTICAL RESULTS FROM MAGNESIUM-BASE SULFITE PULPS

Sample	Yield, %	Klason Lignin, %	Kappa Number	Nu Number
		Cook 1		
1	78.6	26.75	--	152
2	56.5	12.75	78.1	94
3	60.8	17.80	101	113
4	52.2	10.25	66.1	75
5	46.0	7.06	40.2	44
		Cook 2		
1	53.8	10.70	74.5	86
2	51.1	8.80	61.4	71
3	49.9	8.70	62.9	70
4	47.6	6.55	51.8	56
		Cook 3		
1	71.6	25.85	134	149
2	66.3	21.95	122	138
3	60.2	19.40	109	123
4	58.2	13.75	81.4	96
5	54.2	10.25	64.1	80
6	49.9	6.20	45.1	55
7	43.8	6.15	45.1	55

At 145°C. maximum temperature, the pressure in the digester never exceeded 100 p.s.i. It was therefore considered more convenient to use the multiunit digester for further cooks. The same wood and liquor, and in the same ratio, were used. In Table IX are given the experimental conditions for this second cooking series.

TABLE IX

CONDITIONS FOR SECOND SERIES OF SULFITE COOKS

Temp. 145°C. max.; 225 min. to reach max. temp.

Sample	Total Time, min.
Cook 2	
1	390
2	435
3	480
4	525
Cook 3	
1	260
2	300
3	340
4	380
5	440
6	510
7	600

The Kappa and Nu numbers were subjected to correlation analysis. The correlation coefficient was 0.996, the regression line:

$$\text{Kappa} = -2.72 + 0.9025\ \text{Nu}\ ,$$

the standard error of estimate, 2.7, and the relative error of estimate, 3.6%. In Fig. 6 are plotted Kappa numbers against Nu numbers, and the regression line is drawn.

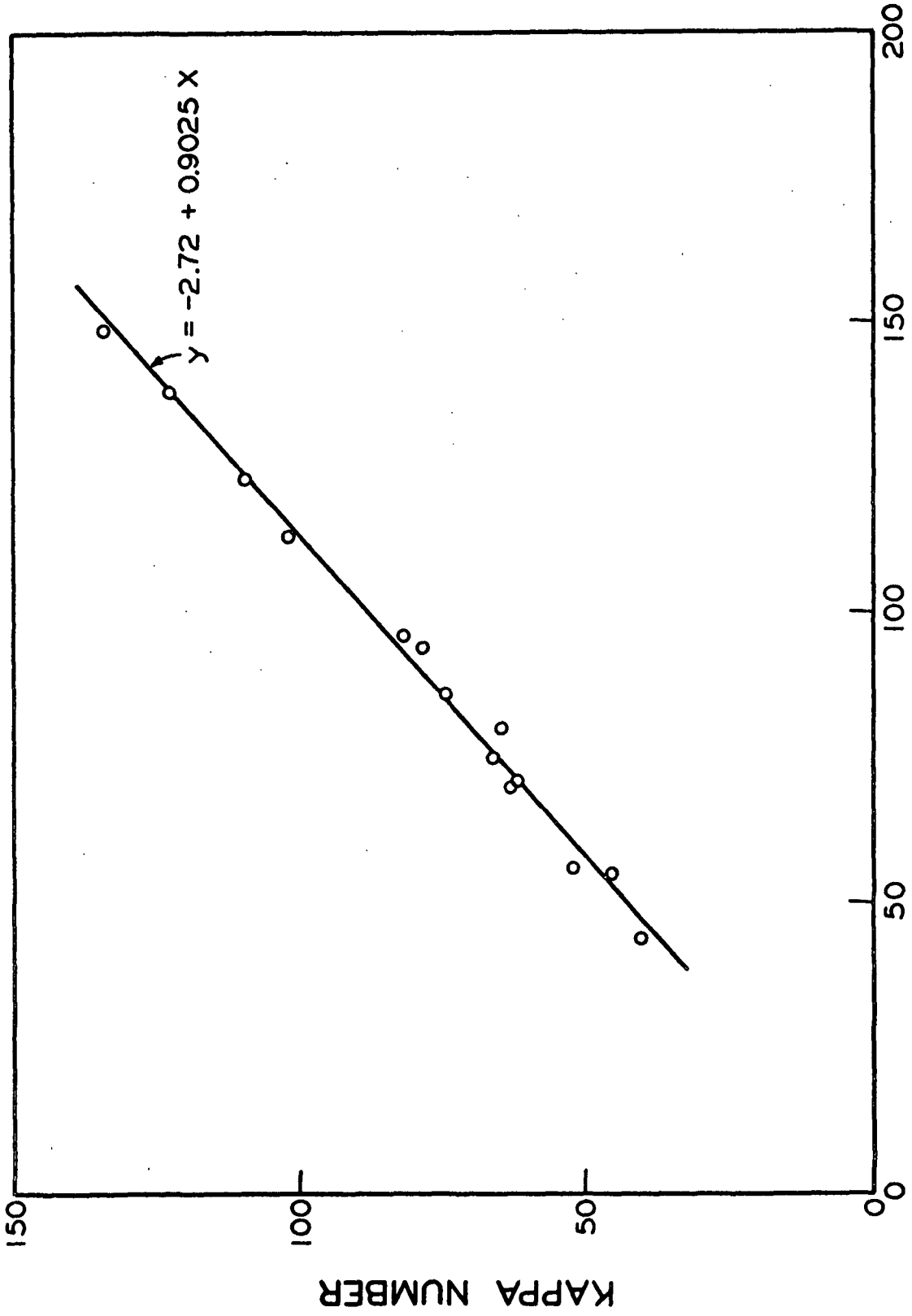

Figure 6. Magnesium-Base Sulfite Pulps, Kappa Number vs. Nu Number

PRELIMINARY STUDIES OF PULP SAMPLING

In past studies of the sheet-forming process, it has been found that in a water-saturated system the compressibility function,

$$C = MP^N \qquad (1),$$

expresses the relationship between the mass of dry fiber in a compressed bed and the compressing pressure, where:

$\underline{C}$ = mass of dry fiber per unit bed volume,

$\underline{P}$ = compressing pressure, and

$\underline{M}$, $\underline{N}$ = constants.

It has been found from experimental data that a plot of log $\underline{C}$ vs. log $\underline{P}$ yields a straight line. Factors such as compression time, fiber structure, fiber properties (lignin content, wood species), and experimental conditions have some bearing on the results and require correctional modification of the equation. Usually these modifications result in only minor alterations of the relationship. Hence, it can be seen that the basic equation, above, can be used without alteration to define for a given pulp the relationship between $\underline{C}$ and $\underline{P}$ under fixed experimental conditions.

Development of an automatic pulp-sampling system to yield a known amount of fiber in the samples is based on Equation (1). In general, the proposed system would consist of a cylinder fitted with a porous-face piston and connected to a drainage septum covered with wire mesh to catch the fibers as the slurry is drained through it. The piston would be driven to a fixed stroke length or until it exerted a fixed compressing pressure upon the pad of fibers between its face and the wire mesh covering the septum. With calibration, the mass of equivalent

dry fiber can be calculated from either the measured pressure at a fixed pad thickness or from the pad thickness at a fixed compressing pressure. Although the general compressibility function has been quite well established in other work at the Institute, its application in this work requires considerable modification of the rather lengthy procedure presently employed to experimentally define the compressibility of a given pulp. Other factors must be investigated also, such as precision and repeatability, the effect of variations in lignin content of the fibers, temperature effects, how pad thickness variations affect precision, and many other mechanical factors that will ultimately influence the design of an automated procedure.

PRESENT PROCEDURE FOR COMPRESSIBILITY TEST

The procedure used at The Institute of Paper Chemistry for measuring the compressibility of wet fiber mats was devised by Ingmanson (1, 2) and further developed in other investigations by Ingmanson and various coworkers (3-5). The apparatus presently used is also essentially that initially designed by Ingmanson. A vertical cross section of the compressibility apparatus is shown in Fig. 7.

After flooding the septum with water from the 500-cc. water reservoir, a slurry containing about 5 grams of pulp is poured into the cylinder with the cover and piston removed. Sufficient water is added to position the water level about an inch below the cylinder top, and the slurry is then briefly stirred with a stirring rod. The piston and the cover to the overflow chamber are inserted and the piston is lowered gently by hand. When the piston rests upon the fibers now formed into a loose mat, it is released and the dial micrometer, which is on a swing arm, is placed over the piston and its foot is placed on top of the piston rod. The piston and piston rod assembly, having a known mass, form the first weight. When the micrometer foot is placed on the piston rod, a timer is started,

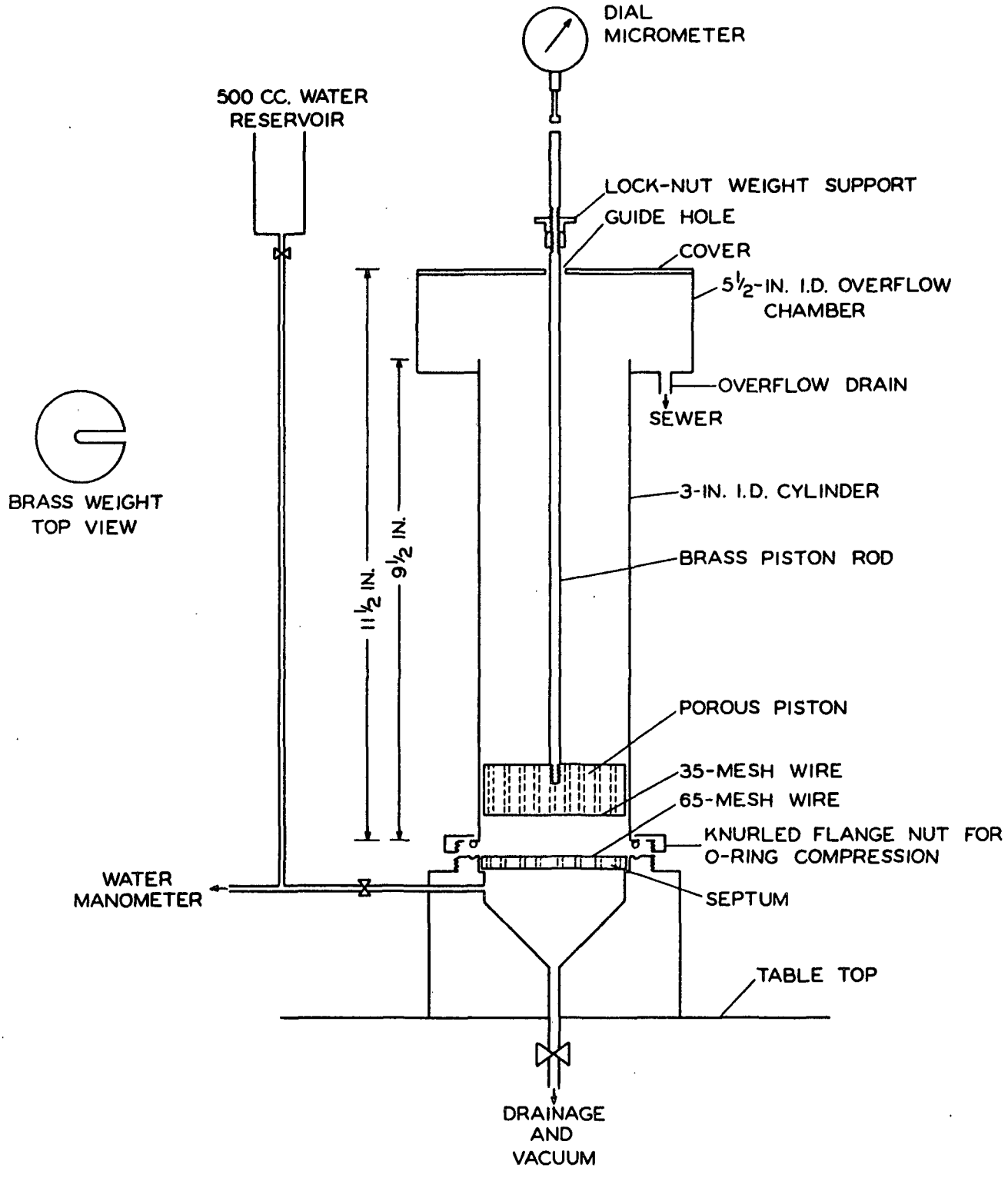

Figure 7. Compressibility Apparatus

and at the end of 12 minutes, the micrometer is read, giving the distance between the piston face and the septum face, which is the pad thickness. At the start of each run, the micrometer is, of course, zeroed with the piston in place and with nothing in the cylinder.

At the end of the 12-minute period, a brass weight similar to the one shown in Fig. 7 is placed on the piston rod so that it rests on the lock nut, and after another 12-minute period the micrometer is read again. This procedure is repeated with five more weights of increasing mass. After the last reading of the micrometer, the water in the cylinder is drained through the piston and the fiber mat, and the piston is removed from the cylinder. The cylinder assembly is detached from the septum assembly and remaining water is drawn from the pad by applying vacuum to the bottom of the septum. The pad is quantitatively removed, placed in a tared weighing bottle, dried at 105°C., and weighed.

From the experimental data (the known mass of each weight, the pad thickness determined by each micrometer reading, and the final dried pad weight), the solids concentration as a function of compacting pressure is established from Equation (2):

$$C_p = \frac{W}{AL} \qquad (2) ,$$

where:

$\underline{C_p}$ = solids at pressure $\underline{P}$ (given by the applied weights), g./cc.,

$\underline{W}$ = dried pad weight, g.,

$\underline{A}$ = empirical constant, and

$\underline{L}$ = measured pad thickness.

If $\ln \underline{C}_{\underline{p}}$ in g./cc. is plotted against $\ln \underline{P}$ in dynes/cm.^{2}, it will be seen that the relationship is linear.

It can be seen that this procedure requires a minimum of an hour and a half to complete and is performed under conditions not at all amenable to direct automation, yet it forms the basis from which an automated sampling procedure may be developed. The present procedure and apparatus were, of course, developed as a tool for laboratory investigation of certain pulp properties, and can be used to yield information essential to the design of an automated device.

EXPERIMENTAL

Using the available apparatus and the procedure just described, seventeen different samples of some of the commercial pulps described in Report One and four laboratory-produced neutral sulfite pulps were subjected to the compressibility test. The kraft pulps selected were made from various wood species, and covered a Kappa number range from 37 to 102. The neutral sulfite pulps were made from gumwood, the cooking conditions for which are given in Table IV.

The complete compressibility data for all twenty-one experiments are given in Table X, where the kraft pulps are identified by the letter K following the sample number, and the neutral sulfite pulps have the letters NS following the sample number. The results for Samples 2K, 8K, 13K, and 17K are illustrated in Fig. 8. The four neutral sulfite pulps ranged in yield from 60 to 90%, and the results for these are illustrated in Fig. 9.

TABLE X

COMPLETE COMPRESSIBILITY DATA FOR UNBLEACHED SOFTWOOD KRAFT PULPS OF VARYING LIGNIN CONTENT

Sample No.	Pad Weight, g.	Pressure, dynes/cm.^{2} x 10^{-3} 8.15 Pad Thickness, in.	8.15 Solids Concn., g./cc.	13.1 Pad Thickness, in.	13.1 Solids Concn., g./cc.	22.9 Pad Thickness, in.	22.9 Solids Concn., g./cc.	37.7 Pad Thickness, in.	37.7 Solids Concn., g./cc.	62.3 Pad Thickness, in.	62.3 Solids Concn., g./cc.	96.4 Pad Thickness, in.	96.4 Solids Concn., g./cc.	145.8 Pad Thickness, in.	145.8 Solids Concn., g./cc.
1K	4.900	1.0080	0.0419	0.8635	0.0489	0.6251	0.0675	0.5070	0.0832	0.4223	0.100	0.3605	0.117	0.3090	0.136
2K	5.195	0.9950	0.0450	0.8335	0.0537	0.6615	0.0677	0.5430	0.0825	0.4475	0.100	0.3755	0.119	0.3180	0.141
3K	5.715	1.0100	0.0488	0.9230	0.0534	0.7425	0.0664	0.6180	0.0798	0.5065	0.0973	0.4285	0.115	0.3635	0.136
4K	4.419	0.6050	0.0130	0.5931	0.0642	0.4900	0.0780	0.4112	0.0930	0.3515	0.108	0.3002	0.127	0.2625	0.145
5K	5.566	0.9920	0.0484	0.8515	0.0563	0.6940	0.0692	0.5780	0.0834	0.4780	0.100	0.4030	0.120	0.3442	0.140
6K	5.150	0.9322	0.0475	0.7858	0.0563	0.6400	0.0691	0.5308	0.0826	0.4401	0.101	0.3711	0.120	0.3190	0.139
7K	4.508	0.8975	0.0434	0.6709	0.0579	0.5451	0.0712	0.4508	0.0861	0.3730	0.104	0.3110	0.125	0.2700	0.144
8K	4.260	0.7640	0.0482	0.6340	0.0580	0.5112	0.0718	0.4245	0.0868	0.3535	0.104	0.2995	0.123	0.2577	0.142
9K	5.090	0.9069	0.0484	0.7765	0.0567	0.6350	0.0691	0.5284	0.0834	0.4329	0.100	0.3703	0.119	0.3142	0.140
10K	5.377	1.0635	0.0435	0.8973	0.0520	0.7151	0.0650	0.5955	0.0779	0.4870	0.0950	0.4111	0.113	0.3530	0.132
11K	4.818	0.9318	0.0446	0.7750	0.0537	0.6200	0.0670	0.5132	0.0810	0.4250	0.0980	0.3568	0.117	0.3025	0.139
12K	4.379	0.8307	0.0454	0.6255	0.0602	0.5130	0.0732	0.4320	0.0872	0.3595	0.105	0.3092	0.122	0.2681	0.141
13K	4.922	0.8585	0.0494	0.7440	0.0570	0.6120	0.0693	0.5110	0.0830	0.4260	0.0995	0.3600	0.118	0.3075	0.138
14K	5.435	0.9980	0.0470	0.8409	0.0560	0.6816	0.0690	0.5698	0.0825	0.4720	0.100	0.4013	0.117	0.3418	0.138
15K	4.633	0.7870	0.0507	0.6618	0.0603	0.5410	0.0738	0.4650	0.0858	0.3790	0.105	0.3250	0.123	0.2790	0.143
16K	3.978	0.8420	0.0408	0.6925	0.0495	0.5549	0.0620	0.4600	0.0748	0.3740	0.0920	0.3150	0.109	0.2670	0.128
17K	5.233	1.0180	0.0443	0.8765	0.0515	0.7170	0.0629	0.5940	0.0759	0.4991	0.0904	0.4190	0.108	0.3611	0.125
18NS	5.030	0.7580	0.0575	0.6565	0.0665	0.5280	0.0830	0.4450	0.0980	0.3760	0.115	0.3260	0.133	0.2835	0.154
19NS	5.484	0.7840	0.0600	0.6223	0.0760	0.5322	0.0890	0.4720	0.1000	0.4118	0.115	0.3760	0.126	0.3300	0.144
20NS	5.901	0.8861	0.0580	0.7665	0.0665	0.6550	0.0780	0.5548	0.0920	0.4790	0.107	0.4100	0.124	0.3615	0.141
21NS	5.090	0.7350	0.0600	0.6425	0.0680	0.5420	0.0810	0.4575	0.0960	0.3868	0.114	0.3355	0.131	0.2920	0.150

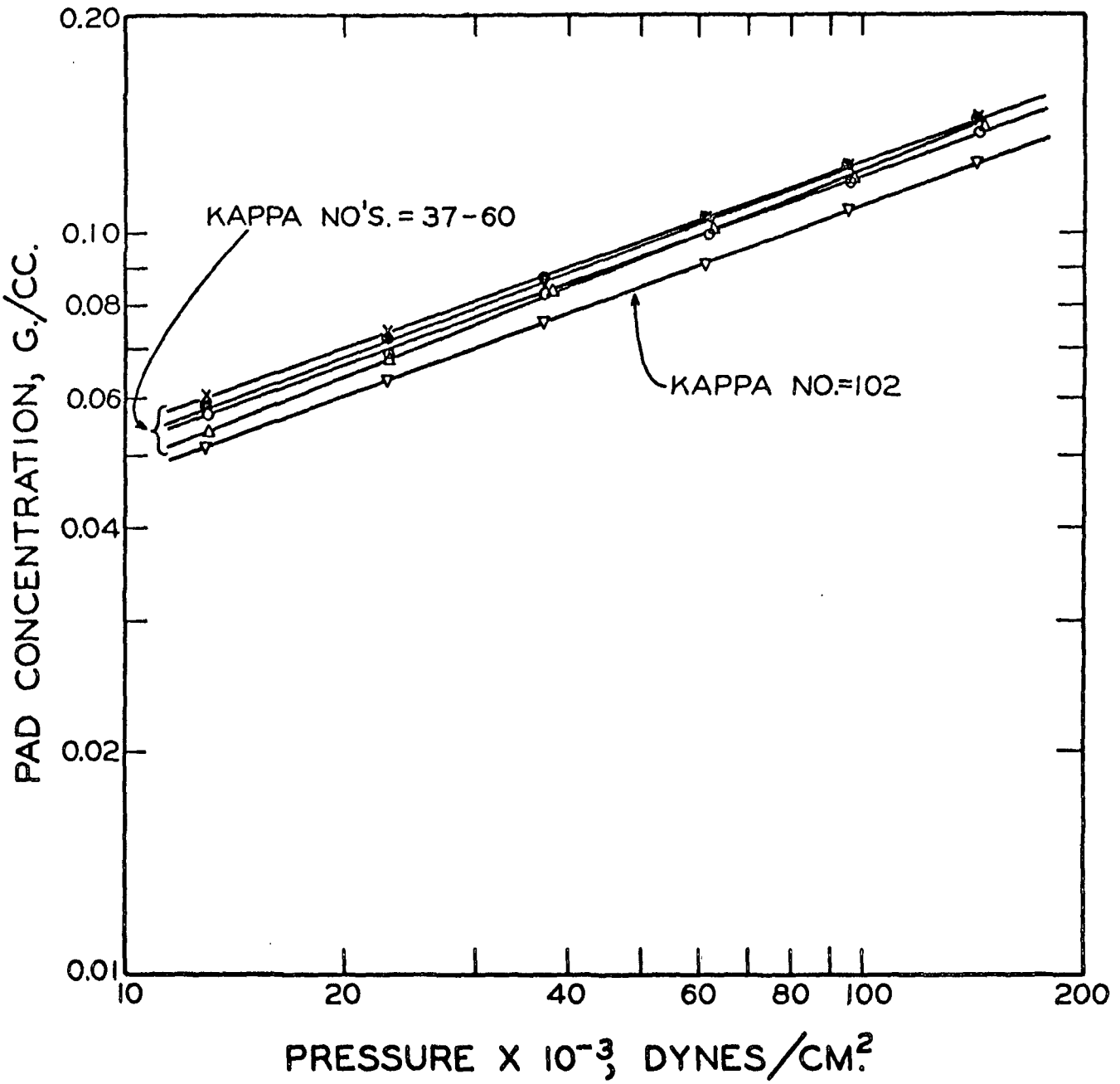

Figure 8. Relationship Between Compressing Pressure and Dry Fiber Content of Compressed Pads of Softwood Unbleached Kraft Pulp

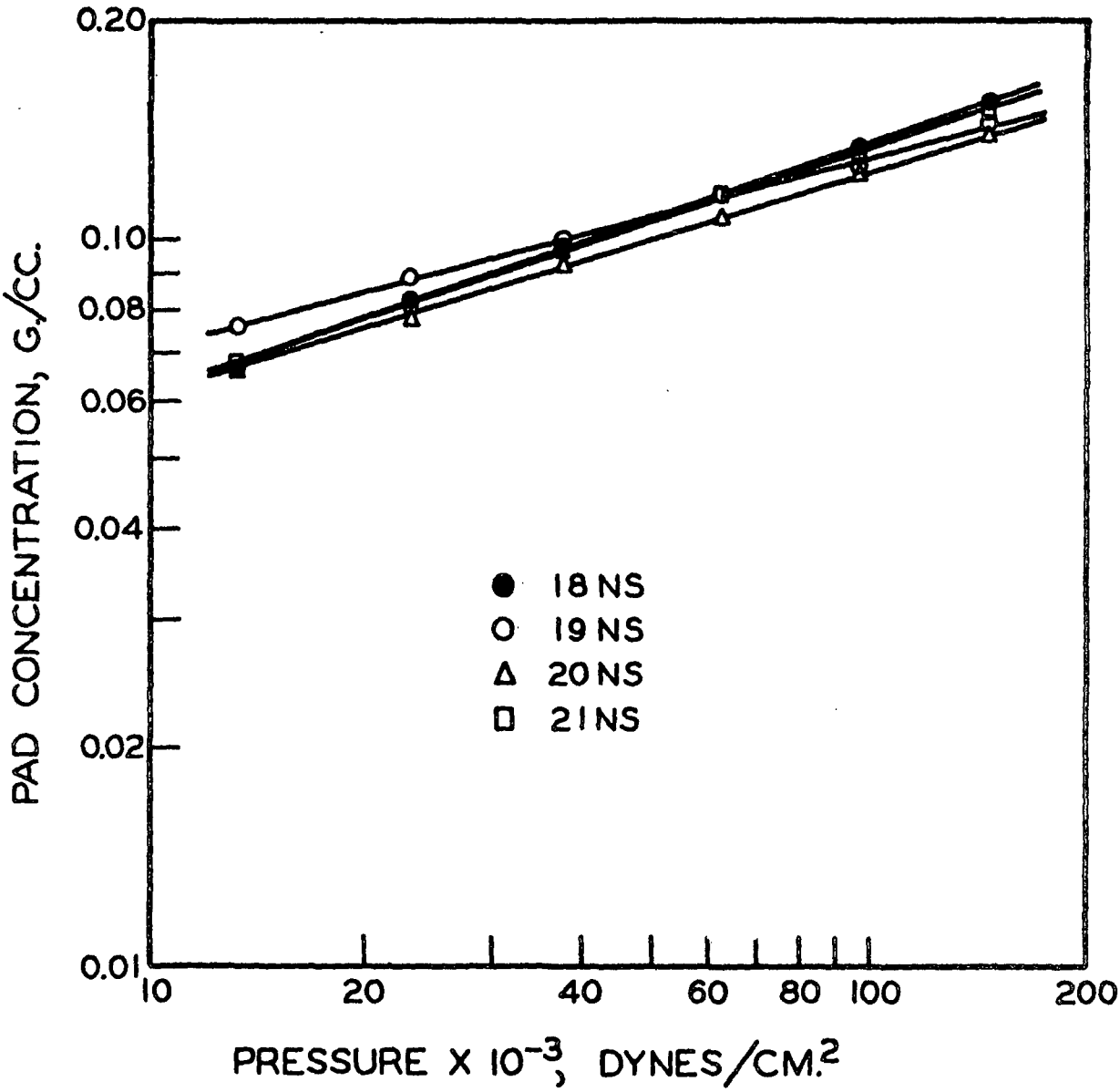

Figure 9. Relationship Between Compressing Pressure and Dry Fiber Content of Compressed Pads of Neutral Sulfite Pulp

One of the kraft pulps was selected for further experiments. The Kappa number of the pulp was 54. Varying amounts of the pulp were placed in the compressibility apparatus, and the six weights were placed upon the piston at 2-minute intervals, the final pad thickness being read when the rate of compression reached an "equilibrium" value of 0.001 inch per minute. The data are listed in Table XI and illustrated in Fig. 10. The regression equation was found to be:

$$W = 0.19 + 15.8L \qquad (3) .$$

This regression line is drawn through the data points in Fig. 4. The correlation coefficient is 0.9998, the standard error is 0.025 gram, which gives a relative error of 1.1%.

A second series of experiments were made with the same pulp, but using only the first three weights, so that the final compacting pressure was only 37.7×10^{-3} dynes/cm.^{2}. Again, the weights were added at 2-minute intervals, and the final reading of pad thickness was made when the rate of compression decreased to 0.001 inch per minute. The experimental data are listed in Table XII and illustrated in Fig. 11. For these experiments, the regression line was found to be:

$$Y = 0.124 + 9.855X \qquad (4) .$$

The correlation coefficient is 0.9996, the standard error is 0.042 gram, which is equivalent to a relative error of 2.1%.

Using the same pulp, a third series of experiments were made in which the total weight, corresponding to 37.7×10^{-3} dynes/cm.^{2}, was placed on the piston at the same time. These results are listed in Table XIII and are plotted in Fig. 12. The regression equation is:

TABLE XI

PAD WEIGHT AND PAD THICKNESS AT 146 x 10^{-3} DYNES/CM.^{2}

Test No.	Pad Thickness, in.	Pad Weight, g.
1	0.1995	3.3407
2	0.1665	2.8505
3	0.1315	2.3170
4	0.1220	2.1212
5	0.1195	2.0851
6	0.0773	1.4021
7	0.0780	1.3756
8	0.1925	3.1893
9	0.2215	3.7194
10	0.2765	4.5693
11	0.3155	5.1352
12	0.0338	0.7171
13	0.0680	1.2804
14	0.0995	1.7745
15	0.0270	0.6073
16	0.0715	1.2976
17	0.0695	1.2915
18	0.0725	1.3432
19	0.0930	1.6450
20	0.1090	1.8900
21	0.1330	2.3064
22	0.1475	2.5255

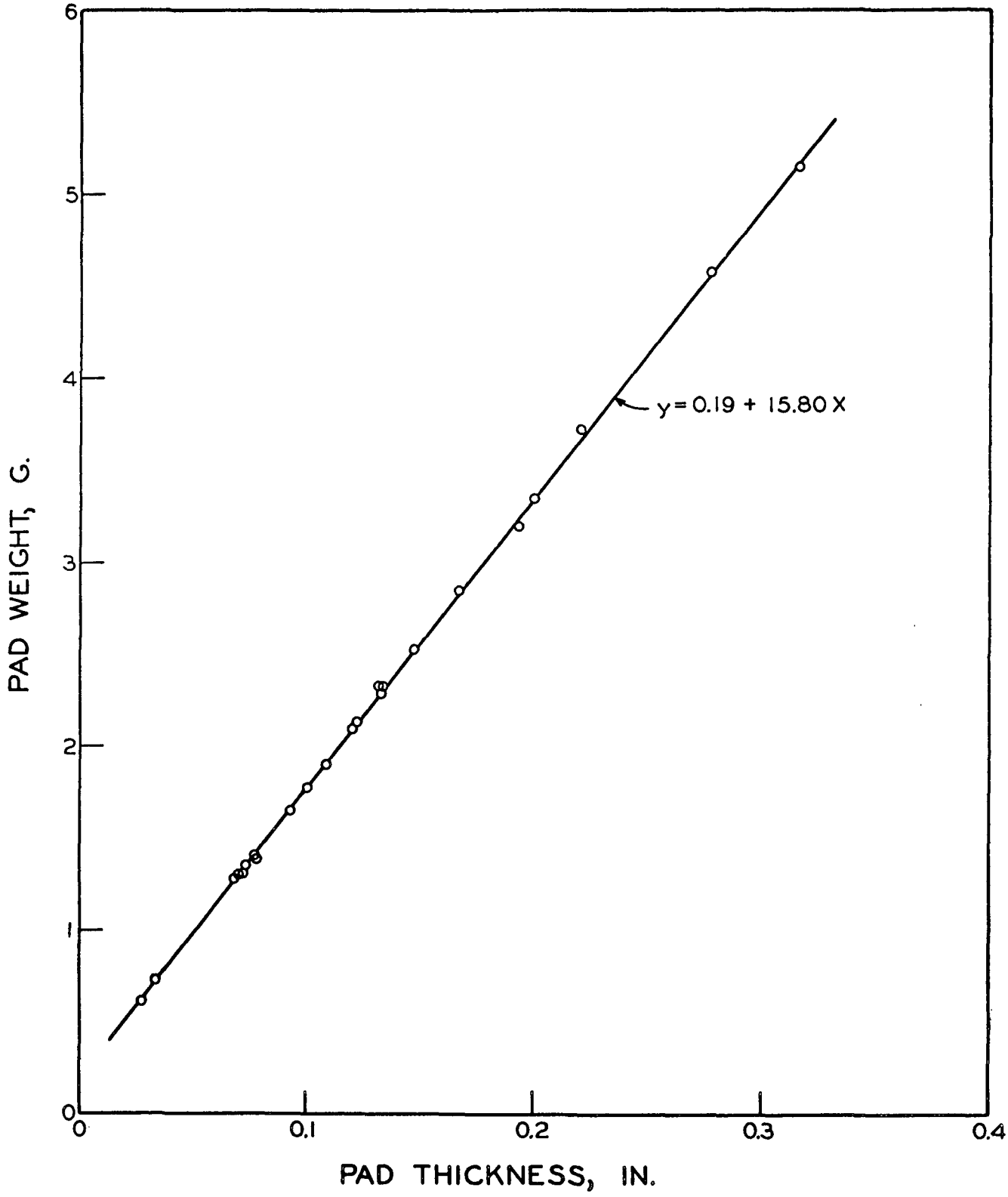

Figure 10. Pad Weight vs. Pad Thickness at 146 x 10^{-3} Dynes/Cm.^{2}

TABLE XII

PAD WEIGHT AND PAD THICKNESS AT 37.7 x 10^{-3} DYNES/CM.^{2}

Test No.	Pad Thickness, in.	Pad Weight, g.
1	0.0450	0.5410
2	0.1200	1.3116
3	0.2630	2.7903
4	0.1705	1.8400
5	0.0600	0.6824
6	0.1222	1.3273
7	0.0840	0.9458
8	0.1160	1.2229
9	0.1152	1.2383
10	0.1435	1.6067
11	0.1192	1.3166
12	0.0579	0.6263
13	0.0325	0.3995
14	0.0465	0.5643
15	0.0825	0.9613
16	0.0965	1.1087
17	0.1980	2.1411
18	0.2485	2.6234
19	0.3490	3.5555
20	0.4390	4.4604
21	0.5400	5.3479
22	0.6538	6.5742

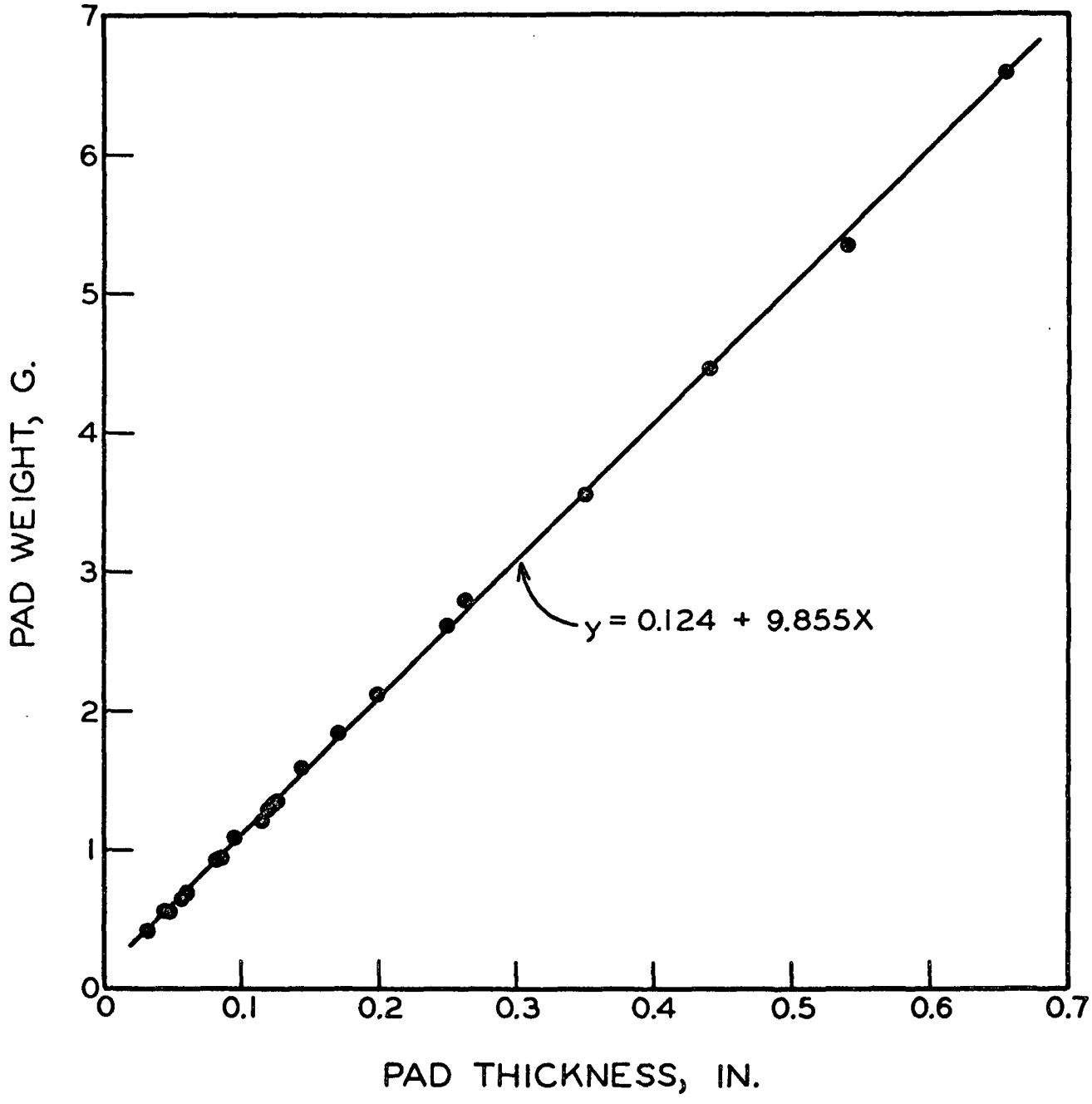

Figure 11. Pad Weight vs. Pad Thickness at 37.7×10^{-3} Dynes/Cm.^{2}

TABLE XIII

PAD WEIGHT AND PAD THICKNESS AT 37.7×10^{-3} DYNES/CM.^{2}
ALL WEIGHTS ADDED AT ONCE

Test No.	Pad Thickness, in.	Pad Weight, g.
1	0.0130	0.2122
2	0.0387	0.4718
3	0.0550	0.6373
4	0.0892	1.0559
5	0.1192	1.3379
6	0.1300	1.4415
7	0.1790	1.9997
8	0.2170	2.4191
9	0.2372	2.5997
10	0.3286	3.5664

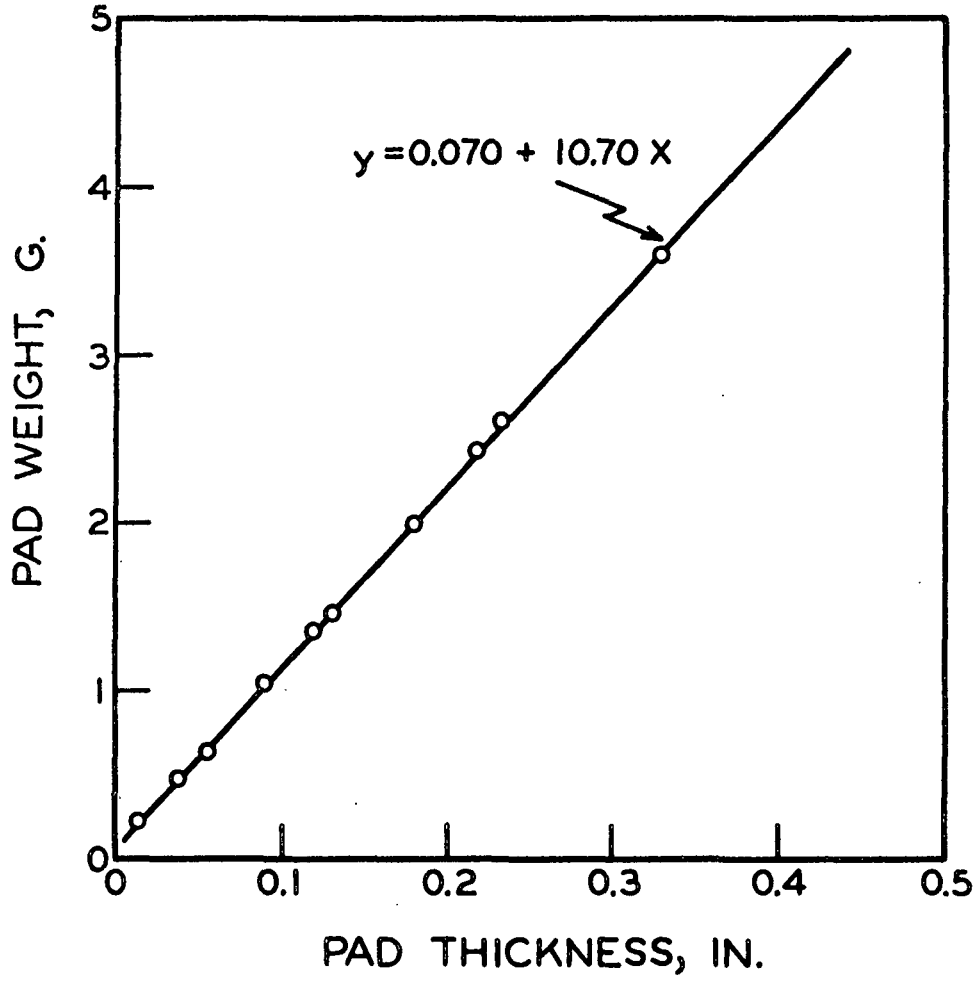

Figure 12. Pad Weight vs. Pad Thickness at 37.7×10^{-3} Dynes per $Cm.^2$; All Weights Added at Once

$$Y = 0.070 + 10.70X \qquad (5) .$$

The standard error is 0.029 gram and the relative error is 1.85%. The correlation coefficient is 0.9996.

DISCUSSION

The data in Table X and in Fig. 8 and 9 show quite clearly that the general relationship between ln C and ln P is linear for a number of different kraft pulps and also for at least one high-yield pulp cooked by the neutral sulfite process.

Figures 10-12 and Tables XI-XIII contain evidence that a linear relationship also exists between the thickness of a compressed pad of fibers and the dry fiber content of the compressed pad under static load conditions. It can be seen also that the precision with which the dry fiber content can be estimated from thickness measurements is within an error of 2%. It was found that in these experiments the time required to reach the arbitrarily chosen "equilibrium" compression rate of > 0.001 in./min. is a function of pad thickness. In the experiments represented in Table XIII, the "equilibrium" value was reached in two minutes or less for Tests 1-3, in 3-4 minutes for Tests 4 and 5, in 4-5 minutes for Tests 6 and 7, and in 5-6 minutes for Tests 7-10.

The significance of the time to "equilibrium" and of the precision of estimating dry fiber content from thickness measurements can be seen from a consideration of possible design features of an automated apparatus. After introduction of a fixed volume of pulp slurry into the cylinder of such an apparatus, the weighted piston could be lowered at a controlled rate until a fiber pad forms. At this point, the weighted piston would be released to compress the pad

to the equilibrium rate of compression, at which point its thickness would be measured. Once the slurry is in the cylinder, the whole process should not take more than three minutes if thin pads are formed.

FUTURE WORK

Based on the results obtained with the Institute's compressibility tester, which produces pads of 3-inch diameter, a smaller apparatus has been designed and is presently under construction. The cylinder is made of precision-bore pyrex tubing, and the supporting section is also made of pyrex. The wire and its support are made of Type 316 stainless steel. The wire and its support are assembled as essentially one piece and nest in the lower part, or supporting member, of the pyrex tube.

The smaller diameter will permit use of amounts of fiber as small as 100 mg., yet will result in pads with thicknesses easily measurable. The pyrex-stainless steel construction permits introduction of nitric acid into the apparatus for conducting the Nu number test on reslurried pads right in the apparatus. Further, the materials of construction permit operation of the system at temperatures above ambient.

The portion of the lower pyrex supporting member below the wire assembly is designed with a low volume for drainage, because it is intended that the nitric acid solution be drained to a colorimeter after an appropriate heating period with the reslurried pulp pad.

The Nu number test requires heating the pulp sample for a period of about eight minutes at 80°C., according to the procedure used in the industrial trial of the manual method. It is not known what effect such high temperatures have on the compression characteristics of fibers, and one of the major efforts in future work will be investigations of temperature effects on pulp compressibility. Also, the Nu number procedure is flexible and amenable to modifications that might be required by the results of the temperature-compressibility studies.

The object will be to establish the optimum conditions compatible with the overall compression-Nu number cycle of operations in the automated apparatus.

Once these basic conditions are established, a semiautomatic system will be assembled to study system response times, accuracy and reproducibility limits, and to obtain data for a fully automated prototype instrument. It is expected that construction of this prototype will begin about the first of 1968 and that it will be ready for industrial trial by May of 1968.

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